



Pollutant emissions during pyrolysis and combustion of waste printed circuit boards, before and after metal removal



Nuria Ortuño, Juan A. Conesa^{*}, Julia Moltó, Rafael Font

Chemical Engineering Department, University of Alicante, P.O. Box 99, 03080 Alicante, Spain

HIGHLIGHTS

- Thermal decomposition of printed circuit boards (with and without metals) is studied.
- Important differences were found at the different experimental conditions.
- Emission of brominated pollutants is much higher than that of chlorinated.
- Metal enhances emission of halogenated compounds.
- An increase in the temperature produces the destruction of pollutants.

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ABSTRACT

The constant increase in the production of electronic devices implies the need for an appropriate management of a growing number of waste electrical and electronic equipment. Thermal treatments represent an interesting alternative to recycle this kind of waste, but particular attention has to be paid to the potential emissions of toxic by-products. In this study, the emissions from thermal degradation of printed circuit boards (with and without metals) have been studied using a laboratory scale reactor, under oxidizing and inert atmosphere at 600 and 850 °C. Apart from carbon oxides, HBr was the main decomposition product, followed by high amounts of methane, ethylene, propylene, phenol and benzene. The maximum formation of PAHs was found in pyrolysis at 850 °C, naphthalene being the most abundant. High levels of 2-, 4-, 2,4-, 2,6- and 2,4,6-bromophenols were found, especially at 600 °C. Emissions of PCDD/Fs and dioxin-like PCBs were quite low and much lower than that of PBDD/Fs, due to the higher bromine content of the samples. Combustion at 600 °C was the run with the highest PBDD/F formation: the total content of eleven 2,3,7,8-substituted congeners (tetra- through heptaBDD/Fs) was 7240 and 3250 ng WHO₂₀₀₅-TEQ/kg sample, corresponding to the sample with and without metals, respectively.

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1. Introduction

Waste from electrical and electronic equipment (WEEE) is growing significantly and causing a huge environmental problem if not dealt with in an appropriate way, besides the enormous resource impact of electrical and electronic equipment (EEE) production (UNEP, 2009). Currently, the available data on e-waste are poor; United Nations University's estimations of the current e-waste arisings across the EU amount to around 8.3–9.1 million tonnes for 2005 (UNU, 2007). The same study forecasts a 2.5–2.7% annual growth for total WEEE (household and non-household), reaching about 12.3 million tonnes by 2020 in these countries.

Printed circuit boards (WCB) are one of the most complex constituents of WEEE, with a mixture of both valuable and/or hazardous

elements. Metals represent up to 40% in weight (including Cu, Al, Fe, Sn, Co, In, Sb and precious metals like Ag, Au, Pd and Pt), ceramic material up to 30% (mainly SiO₂ and Al₂O₃), and plastic content corresponds to the remaining 30% (Li and Zeng, 2012). In addition, tetrabromobisphenol A (TBBPA) is predominantly used as reactive flame retardant in rigid FR-4 printed circuit boards, incorporated through chemical reactions with the epoxy resin (US EPA, 2009).

According to Guo et al. (Guo et al., 2009), the WCB components are usually divided into metallic fractions (MFs) and non-metallic fractions (NMFs), which consist of metals (mainly copper) in the first case and a mixture of reinforcing materials, thermosetting resins, brominated flame retardants (BFR) and other additives in the second case.

Extensive investigation has been carried out on pyrolysis as a recycling technique for waste WCB without previous separation of the metallic and non-metallic fractions. Chiang et al. (Chiang and Lin, 2014; Chiang et al., 2010) carried out the pyrolysis of crushed WCB between 200 and 500 °C and analyzed the composition of residue, liquid

^{*} Corresponding author. Tel.: +34 965903400; fax: +34 965903826.
E-mail address: ja.conesa@ua.es (J.A. Conesa).

and gaseous fractions. Chien et al. (Chien et al., 2000) studied the distribution of Br in pyrolysis products by using a fixed-bed reactor at 350–800 °C and thermogravimetry, and found that it mainly evolved as HBr and bromobenzene in the product gas. De Marco et al. (de Marco et al., 2008) conducted pyrolysis experiments at 500 °C on four different WEEE samples (polyethylene wires, table phones, mobile phones and printed circuit boards), with a focus on the solid and liquid fractions. Guo et al. (Guo et al., 2014) studied the pyrolysis of large-size FR-4 WCB at 500 °C in a fixed-bed reactor at 500 °C, obtaining 71.6 wt% of solid residue, 18.2 wt% of tar and 10.17 wt% of gas. Other authors (Hall and Williams, 2007a, 2007b; Quan et al., 2010) reported on the pyrolysis at high temperature (700–800 °C) as a feasible way to recover the organic, metallic and glass fiber material from circuit boards from different appliances (televisions, computers, and mobile phones). Jie et al. (Jie et al., 2010, 2008) performed the pyrolysis of WCB from waste personal computers, at temperatures between 300 and 700 °C for 30 min, and suggested that the resulting pyro-oils and gases could be used as fuels or chemical material resource. Long et al. (Long et al., 2010) proposed a combination of vacuum pyrolysis and mechanical processing using a pilot-scale fixed bed reactor to recycle the different fractions of waste WCB (i.e. organic resins, copper and glass fiber).

Watanabe et al. (Watanabe et al., 2008) and Sakai et al. (Sakai et al., 2001) conducted combustion experiments of waste WCB in a pilot-scale incinerator equipped with a flue gas treatment system. They observed the formation of brominated, chlorinated and mixed halogenated dioxins and furans, although the overall destruction rate was higher than 90% in flue gas at the final exit.

Concerning the thermal treatment of metal-free samples from waste WCB, some authors analyzed the pyrolysis and/or combustion products. Blazsó et al. (Blazsó et al., 2002) studied the potential of different inorganic solids of basic character as dehalogenation agents in the pyrolysis of electronic scrap (an electronic junction and a printed circuit board without metals) at 450 and 600 °C. Barontini et al. (Barontini and Cozzani, 2006; Barontini et al., 2005) used thermogravimetric analysis and a laboratory-scale fixed-bed reactor to study the thermal degradation patterns of metal-free samples from epoxy resin circuit boards, both in inert and oxidizing atmospheres. The findings of these works were compared with those corresponding to the degradation of a TBBPA containing paper-phenol laminate by Grause et al. (Grause et al., 2008), who pyrolyzed the sample both in a thermogravimetric analyzer and in a quartz glass reactor (40–1000 °C). Quan et al. (Quan et al., 2012) used TG-FTIR (thermogravimetry with Fourier transformed infrared) and Py-GC/MS (Pyrolysis with gas chromatography and MS detector) techniques to analyze the pyrolysis of metal-free WCB waste at 600 °C.

Despite the considerable amount of research carried out on the decomposition and products obtained during thermal treatment of used WCB, less attention has been paid to the toxicity of the gaseous products emitted. There can be a potential for emissions of brominated dioxins and furans or other by-products when products containing TBBPA are combusted during end-of-life processes (US EPA, 2009). Only some authors (Duan et al., 2011, 2012; Gullett et al., 2007; Lai et al., 2007) characterized the emission of PBDD/Fs (brominated dioxins and furans) from pyrolysis or combustion of such wastes, and, as stated by Duan et al. (Duan et al., 2011), further research is needed on the influence of metals in the emissions of halogenated pollutants from WCB waste incineration.

Our group has already reported on the combustion and pyrolysis emissions from obsolete mobile phones, including printed circuit boards, mobile cases and a mixture of both materials (Moltó et al., 2011, 2009), but analyzing only the chlorinated compounds, including PCDD/Fs. The aim of the present study is to characterize the emissions from thermal degradation of waste WCB in an exhaustive way, especially regarding the potential formation of PBDD/Fs and the influence of the metal presence. In this way, the study comprises the analysis of gases, halogens and hydrogen halides, carbon oxides, light hydrocarbons,

polycyclic aromatic hydrocarbons (PAHs), chlorinated phenols (ClPhs), chlorinated benzenes (ClBzs) and brominated phenols (BrPhs), among other semivolatile compounds, as well as polybromo- and polychlorodibenzo-p-dioxins and furans (PBDD/Fs and PCDD/Fs) and dioxin-like polychlorobiphenyls (dl-PCBs).

2. Materials and methods

2.1. Material

Printed circuit boards from 10 different waste mobile phones (approximately 100 grams) were separated and crushed to fine dust (sample named “WCB”, corresponding to the whole printed circuit boards), using a vibratory disc mill by Herzog, HSM 100 (Osnabrück, Germany). In order to obtain a metal-free fraction, a part of “WCB” sample was treated with a dilute aqueous solution of HCl and H₂O₂, followed by washing with deionized water and drying at 110 °C (sample named “nmf-WCB”, corresponding to the non-metallic fraction).

The characterization of both samples and a thermogravimetric study about the thermal decomposition of these samples under inert and oxidative atmospheres was previously published (Ortuño et al., 2013). Using a CHNS analyzer, a carbon content of 20.4 and 36.4 wt% was found for the “WCB” and the “nmf-WCB”, respectively. The effectiveness of the acid washing treatment was confirmed by X-ray fluorescence, with the “WCB” sample showing a copper content of 24.2 wt% versus 0.50 wt% for the “nmf-WCB”. Not only Cu, but also Ca, Al, Pb, Sn, Ni and Fe showed a significant decrease in the “nmf-WCB” and, as a consequence of the removal of the metallic content, the concentration of the remaining elements increased. It must be emphasized that the amounts of Br and Cl, change from 5.7 and 0.13 wt% in the “WCB” sample to 12.2 and 1.04 wt% in the washed sample (Ortuño et al., 2013).

2.2. Experimental setup

Pyrolysis and combustion runs were conducted with both samples at two different temperatures (600 and 850 °C), using a tubular quartz reactor located inside a horizontal laboratory furnace described in detail elsewhere (Aracil et al., 2005a). For each run, synthetic air (combustion runs) or nitrogen (pyrolysis runs) was introduced in parallel flow with respect to the sample, at a constant flow of 300 mL/min (1 atm, 20 °C). With this gas flow rate, the gas residence time at the nominal temperature was calculated to be 4.9 s at 600 °C and 3.5 s at 850 °C. The higher temperature (850 °C) was chosen because the EU incineration directive (European Council, 2000) sets a minimum of two seconds at this temperature for the post-combustion zone of an incinerator, whereas the lower temperature (600 °C) is enough to achieve the thermal decomposition of the samples (Ortuño et al., 2013) and represents low temperature zones in the combustion chamber.

The sample was placed in a holder (quartz boat), which was introduced into the reactor at a constant speed (1 mm/s), once the set temperature had been reached, and maintained inside the reactor for 10 min, while the compounds leaving the laboratory reactor were sampled for subsequent analysis. A packing of quartz rings was placed at the end of the reactor to avoid gas bypass, ensure good mixing of the gases from the primary decomposition of the samples and allow further reactions (Aracil et al., 2005b).

A bulk air ratio was defined (Aracil et al., 2010) as the ratio between the actual oxygen flow and the stoichiometric oxygen flow necessary for complete combustion. The chosen sample amounts correspond to an air ratio of 0.95, slightly substoichiometric oxygen conditions, favoring the formation of compounds of incomplete combustion, in order to simulate the operation of the system under adverse conditions and poor combustion. This corresponds to 75 mg of “WCB” and 40 mg of “nmf-WCB”.

2.3. Analytical procedure

Four different runs were carried out for each experimental condition and each sample, as well as a blank, due to the different sampling and analyses techniques used to quantify the following groups of target compounds.

For quality control, our laboratory participates in an annual intercalibration study on the analysis of PCDD/Fs giving very good results. Furthermore, blank runs are done for each experimental conditions, where the main compounds are analysed with no sample introduced to the system. A program of calibration of the GC/FID and GC/TCD system is running on our laboratory, with recalibrations every three months.

2.3.1. Hydrogen halides and halogen gases

For determining the emissions of inorganic bromine (HBr and Br₂) and chlorine (HCl and Cl₂), the gases were passed through two consecutive impingers containing 0.1 N sulfuric acid and 0.1 N sodium hydroxide dilute solutions, in accordance with the U.S. EPA method 26 (US EPA, 1994a). The hydrogen halides were solubilized in the acidic solution, whereas the halogens passed through to the alkaline solution where they are hydrolyzed. The solutions were analyzed using a Dionex DX500 ion chromatograph.

2.3.2. Gases and volatile compounds

Gases and volatile compounds were collected in Tedlar® bags (Restek, USA) at the reactor exit. A gas chromatograph coupled to a thermal conductivity detector (GC-TCD) was used to analyze carbon oxides, oxygen and nitrogen, using an Alltech CTR I column. A gas chromatograph with a flame ionization detector (HRGC-FID) was used for the analysis of light hydrocarbons (methane to xylenes), using an Alumina KCl Plot capillary column. The identification and quantification of these compounds was carried out by external standard calibration.

Other non-condensable gases were analyzed using a DB-624 capillary column by gas chromatography coupled to mass spectrometry (HRGC-MS) in the SCAN mode. An external standard calibration was carried out using EPA 502/524.2 VOC Mix (Supelco, USA).

2.3.3. Semivolatile compounds

Amberlite® XAD-2 resin was used to adsorb the semivolatile compounds in the flue gases. Different internal standards (deuterated PAH Mix 26 from Dr. Ehrenstorfer, Germany and ¹³C-labeled bromophenols MBRPS, chlorophenols MCPS and chlorobenzenes MCBS from Wellington Laboratories) were added to the resin before it was extracted with dichloromethane/acetone (1:1 vol.) by accelerated solvent extraction (Dionex ASE® 100). The extracts were concentrated to approx 1 mL and a recovery standard was added (anthracene-d₁₀ from AccuStandard, Inc., USA). These compounds, including polycyclic aromatic hydrocarbons (PAHs), were analyzed using HRGC-MS in the SCAN mode (35–550 amu) with an Agilent HP5-MS (30 m × 0.25 mm i.d. × 0.25 μm) capillary column, using the U.S. EPA method 8270D (US EPA, 2007) for reference. Native standards were used for the identification and quantification of the 16 priority PAHs established by the U.S. EPA (US EPA, 1998), whereas other semivolatile compounds were identified by comparison with the NIST mass spectral database, interpolating between the response factors from the two nearest deuterated standard for semi-quantification.

Chlorinated phenols (ClPhs), benzenes (ClBzs) and brominated phenols (BrPhs) were specifically analyzed in the SIR mode, and quantified by internal standard calibration, in a similar way as the 16 PAHs. The identification of each isomer was confirmed by checking the ratio between the areas of the primary and the secondary ions.

2.3.4. PBDD/Fs, PCDD/Fs and dl-PCBs

These compounds were also collected with XAD-2 resin in a separate run. ¹³C-labeled internal standards were added to the resin prior to extraction, which was performed with two different solvents

(dichloromethane and toluene) in subsequent steps (Wyrzykowska et al., 2009). The extracts were concentrated in a rotary evaporator, diluted in n-hexane and divided in two halves. One-half of the extract (used for PCDD/Fs and dl-PCBs determination) was purified and fractionated using an automated Power Prep® system with silica, alumina and active carbon columns. For the second half of the extract (used for PBDD/Fs analysis), dichloromethane was used to elute the alumina column (instead of the 50% hexane-dichloromethane used in the first case) and the carbon column was omitted, as recommended to enhance the recoveries of highly brominated PBDD/Fs (Wyrzykowska et al., 2009).

The different fractions were concentrated in nonane and the corresponding recovery standards were added. The samples were analyzed by HRGC-HRMS using an Agilent HP5890 gas chromatograph equipped with programmable temperature vaporization (PTV) inlet, coupled to a Micromass Autospec Ultima-NT mass spectrometer. An Agilent DB5-MS chromatographic column (60 m × 0.25 mm i.d. × 0.25 μm) was used for the analysis of PCDD/Fs and dl-PCBs, whereas PBDD/Fs were analyzed using a Restek TRB-Meta X5 column (15 m × 0.25 mm × 0.25 μm). The analyses were performed following the requirements of the U.S. EPA method 1613 (US EPA, 1994b) for dioxins and method 1668C (US EPA, 2010) for dl-PCBs.

The recoveries found for the ¹³C-labeled PCDD/Fs (from 52% to 112%), met the criteria of the standard method. The recoveries of the ¹³C-labeled PBDD/Fs (from 21% to 133%) were also between the acceptable limits, except for ¹³C-OBDD/F, which are more prone to degrade and presented recovery values lower than 20% and are not reported here. The recoveries of all ¹³C-PCBs were well within the limits (between 51% and 144%).

Isotopically labeled standards were obtained from Wellington Laboratories (EPA-1613 solutions for PCDD/Fs and WP-CVS solutions for dl-PCBs) and Cambridge Isotope Laboratories (EDF-5407, -5408, -5409 and EF-5410 for PBDD/Fs). All solvents (acetone, dichloromethane, toluene, n-hexane, and ethyl acetate) for the organic trace analysis were purchased from Merck (Germany).

Throughout the experimental process (sampling, extraction, purification, concentration and analysis) the samples were protected from light, in order to prevent photodegradation of the brominated compounds.

3. Results and discussion

3.1. Halogen gases and hydrogen halides

The emissions of inorganic bromine and chlorine are shown in Table 1. Yields of HBr + Br₂ represent 24–28% of initial bromine in the “WCB” sample at 600 °C, reaching 32–37% at 850 °C, whereas for the “nmf-WCB” 39–40% of the bromine content is emitted as HBr + Br₂ at the lower temperature and 49–53% at the higher one. A similar trend is observed for HCl + Cl₂ emissions, which show an increase with temperature.

No significant differences are observed between pyrolysis and combustion experiments, thus the presence of oxygen did not significantly affect the conversion of bromine from the sample to HBr + Br₂ or chlorine to HCl + Cl₂. For both elements, emissions of hydrogen halides are higher than the corresponding halogen gases. In combustion runs, HBr can be oxidized by oxygen to form Br₂, as would occur with HCl by the Deacon reaction; in this study the X₂/HX ratios show only a slight increase at oxidizing atmospheres, probably due to the short residence time of gases in the reactor, not enough to reach chemical equilibrium (Jin et al., 2011).

3.2. Gases and volatile compounds

Table 1 also presents the results of carbon oxides and light hydrocarbons identified by GC-TCD and GC-FID in pyrolysis and combustion

Table 1
Yields of gases and volatile compounds during thermal decomposition (P-pyrolysis, C-combustion) of printed circuit board samples “WCB” and the non metallic fraction “nmf-WCB”.

EXPERIMENT	P600		C600		P850		C850	
SAMPLE	WCB	nmf-WCB	WCB	nmf-WCB	WCB	nmf-WCB	WCB	nmf-WCB
COMPOUND	mg compound/kg sample							
Analysis by ionic chromatography								
HBr	14,900	46,300	12,700	45,900	20,200	58,100	11,800	59,600
Br ₂	1200	1600	1000	3700	1100	2800	6700	5800
HCl	500	4900	400	5300	800	5800	500	6500
Cl ₂	200	400	100	500	300	500	100	300
Analysis by GC-TCD								
CO	–	–	89,000	288,000	–	–	94,800	295,600
CO ₂	18,500	51,200	441,600	595,000	31,900	57,500	677,400	506,200
R _{CO} = CO/(CO + CO ₂)	0	0	0.17	0.33	0	0	0.12	0.37
Analysis by GC-FID								
methane	3570	8540	2910	8310	11,000	23,300	30	30
ethane	590	1530	–	–	90	–	–	–
ethylene	1370	2340	930	1540	3550	6430	–	–
propane	220	520	–	–	–	–	–	–
propylene	2070	4310	310	340	1140	2030	–	–
acetylene	–	–	330	830	780	1310	–	150
n-butane	–	–	–	–	–	270	–	–
isobutene	260	330	–	–	–	–	–	–
cis-2-butene	150	340	–	–	–	–	–	–
propyne	170	360	120	250	270	570	–	–
2-butyne	–	–	–	–	130	240	–	–
n-hexane	220	290	–	–	2430	3060	–	–
benzene	1060	1910	650	1290	13,800	24,500	–	–
toluene	1050	1600	–	1070	3350	7240	–	–
xylene (p-,m-,o-)	–	–	–	–	610	1120	–	–
Analysis by GC-MS								
bromomethane	1650	5220	200	3740	–	–	–	–
acetone	2350	5340	–	5490	–	4330	–	2220
cyclopentadiene	–	–	–	–	4710	8190	–	–
acetonitrile	–	450	–	–	470	1240	–	–
acrylonitrile	–	560	–	–	620	790	–	–
cyanogen bromide	–	–	–	–	–	–	160	750
ethynylbenzene	–	–	–	–	450	970	–	–
indane	–	–	–	–	40	–	–	–
1-chloroindane	–	–	–	–	370	750	–	–

(–): not detected or <10 mg/kg

experiments. Aliphatic hydrocarbons (C₁ to C₆) were identified, as well as aromatic hydrocarbons (benzene, toluene, and xylenes).

Regardless of the sample, CO and CO₂ were the main gaseous compounds, which Hall et al. (Hall and Williams, 2007b) attributed to the decomposition of the epoxy group or the calcium carbonate fillers. The CO/(CO + CO₂) ratio is higher for the sample without metal, and this can be explained by its higher halogen content and the inhibition effect of halogen in CO oxidation (Wang and Anthony, 2009). As observed in a previous work on tetrabromobisphenol A degradation (Ortuño et al., 2014), the combustion runs at both temperatures yield a similar CO/

(CO + CO₂) ratio, due to the unfavorable formation of CO₂ versus CO in the presence of bromine.

The main light hydrocarbons (shown in Table 1) are methane, ethylene, propylene, benzene and toluene, which show similar trends for both samples. Yields are higher under pyrolytic conditions, since these compounds are easily oxidized in the presence of oxygen (Conesa et al., 2009; Conesa et al., 2000); these are considered final products from cracking reactions occurring at high temperatures, and show a maximum at 850 °C, as also observed by Moltó et al. (Moltó et al., 2011, 2009). The yields obtained for sample “nmf-WCB” are

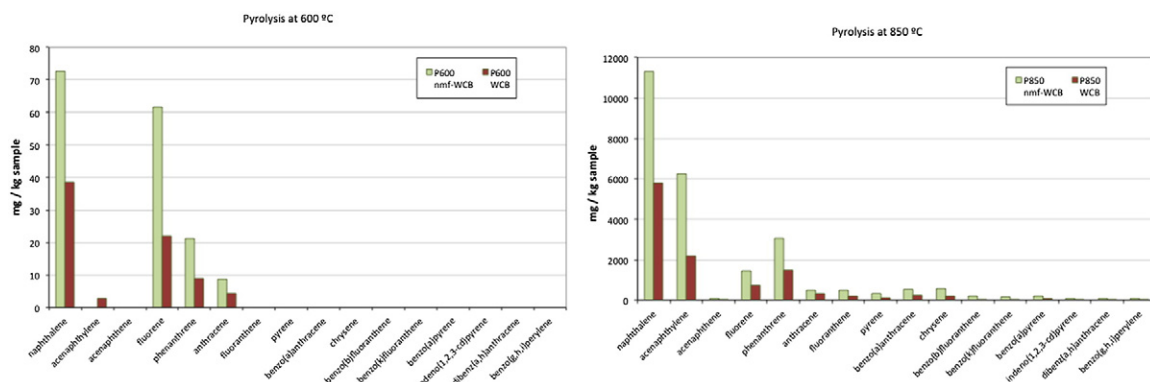


Fig. 1. Yields of 16 priority PAHs during pyrolysis of printed circuit boards with and without metals (“WCB” and “nmf-WCB” samples) at two different temperatures.

approximately twice that of the original sample “WCB”, and this can be due to the fact that the polymer content in the “nmf-WCB” is approximately twice the polymer content in the “WCB” sample. A similar behavior was observed in a previous work, when comparing the emissions of volatile compounds from electronic wastes (mix of circuit board and mobile phone case) and a printed circuit board alone (Moltó et al., 2009).

Other compounds, such as bromomethane and cyclopentadiene are also emitted in high amounts and were detected by GC-MS. Significant amounts of acetone were also observed, which has been reported to be a pyrolysis product of the 2-hydroxypropyl ether segment of epoxy resins (Blazsó, 1991).

3.3. Semivolatile compounds and PAHs

The yields obtained for the 16 priority PAHs and other semivolatile compounds detected by GC-MS in the Scan mode can be found in Table S1 in the Supporting Information (SI). Data corresponding to the emissions of the 16 priority PAHs in pyrolysis are shown in Fig. 1.

Both samples follow similar trends for each experimental condition, with the highest semivolatile yields observed in the pyrolysis run at 600 °C. In order of abundance, phenol, benzofuran and styrene are the most abundant products, detected in all runs, except in the combustion at 850 °C. Apart from these, some of the most important degradation products consist of substituted monoaromatic compounds (i.e. methylated and brominated phenols and benzene derivatives), as well as methylated benzofurans and naphthalenes. These are mainly incomplete combustion compounds, produced by cracking and pyrosynthesis reactions, favored at lower temperatures and oxidized in combustion runs (Conesa et al., 2009). In fact, despite the slightly substoichiometric conditions, in the experiments of combustion at high temperature (850 °C) these compounds were virtually destroyed.

When comparing both samples, yields are higher for the decomposition of the “nmf-WCB”, which has twice the concentration of polymer with respect to the “WCB”, as stated previously.

Based on studies on the oxidative and pyrolytic degradation of 2-BrPh, Evans and Dellinger also found that the maximum formation yield of phenol occurred at 600 °C, and that this was likely due to the exothermic displacement of Br[−] by H⁺ (Evans and Dellinger, 2003, 2005). As observed in the present study, they also reported that the formation of benzene occurred at lower yields and higher temperatures than the formation of phenol, and that this was consistent with the more endothermic displacement of OH[−] by H⁺ from phenol to form benzene, in comparison to the previous mechanism proposed for the formation of phenol.

In pyrolysis at 600 °C, the less severe conditions, both samples emitted mono-, di- and tribromobisphenol A, which are thermally unstable products (neither detected at 850 °C nor in the presence of oxygen) from the primary decomposition of the brominated epoxy resin, and were also detected under the same operation conditions during the thermal degradation of TBBPA (Ortuño et al., 2014).

With respect to the PAHs analyzed (from two to six aromatic rings), yields show a maximum in the experiment of pyrolysis at 850 °C, followed by pyrolysis and combustion runs at 600 °C, whereas none of them was detected in the combustion run at the higher temperature. The most abundant were naphthalene, followed by acenaphthylene, fluorene and phenanthrene. As observed in previous studies, naphthalene is the most abundant PAH formed in the thermal degradation of many different materials (Conesa et al., 2009).

Based on the high amount of cyclopentadiene found in the pyrolysis at 850 °C (see Table 1), which coincides with the maximum formation yield of PAHs, a possible pathway for the formation of naphthalene could be the combination and rearrangement of two cyclopentadienyl radicals, which in turn are formed by CO elimination from phenoxy radicals (Melius et al., 1996). In combustion runs, cyclopentadienyl radicals are oxidized, and the yield of naphthalene decreases significantly.

Yields of PAHs are shown in Fig. 1 for the pyrolysis runs, where similar patterns can be observed for both samples, although the amounts emitted from the non-metallic fraction are approximately twice as high as those from the whole printed circuit board, probably due to the higher polymer content of “nmf-WCB”.

At a set temperature, a great decrease in the total yield of semivolatile compounds was observed from pyrolysis to combustion; as expected, oxygen favored oxidative reactions of pyrolytic products, leading to a decline in their yields.

3.4. Chlorobenzenes, chlorophenols and bromophenols

Relatively low quantities of chlorinated benzenes and phenols were detected (Table S2 and Table S3 in Supporting Information). Total yields of chlorinated benzenes were almost negligible, and varied between 0.01 and 17 mg/kg sample for “WCB” samples and between 0.42 and 34 mg/kg sample for “nmf-WCB”, with mono-, di- and trichlorinated congeners as the most abundant. In pyrolysis, an increase of yields with temperature was observed, whereas the behavior was the opposite in combustion runs. Apart from monochlorinated benzene being the most abundant, no formation pattern is observed for these compounds.

Yields of chlorinated phenols were remarkably higher at 600 °C, obtaining 13 mg/kg sample for the “WCB” sample under both atmospheres, and 114–175 mg/kg sample for the non-metallic fraction in pyrolysis and combustion runs, respectively. It was observed that, at a given temperature, the presence of oxygen did not significantly affect yields.

Considering the runs at 600 °C, monochlorinated congeners were the most abundant (especially 2-ClPh, and 4-ClPh to a lesser extent), followed by 2,4- and 2,6-diClPh. Predominance of these congeners can be explained by the ortho/para directing properties of the OH group in the electrophilic aromatic chlorination of phenol (found in high yields in the runs at 600 °C). These congeners seem to be the most thermodynamically stable in their homologue groups and were found to be dominant in flue gas from municipal waste incinerators (Ballschmiter et al., 1988).

Both samples exhibit similar profiles, but the detected amounts for the “nmf-WCB” are on average 10 times higher than the ones observed for the whole printed circuit board. This can be explained by the difference in the initial chlorine content of the two samples, which results in about 10-fold higher amounts of available chlorine in the form of HCl and Cl₂ for the “nmf-WCB” sample. Emission of phenol was also remarkably higher for this sample in all runs (see Table S1).

Table 2 shows the results of the isomer specific analysis of brominated phenols for all runs. As in the case of chlorinated phenols, monosubstituted congeners predominate, followed by di- and tribrominated phenols, but yields are one or two orders of magnitude higher than for their chlorinated congeners. The highest yields are also observed at 600 °C, being higher in oxidative conditions with respect to the pyrolytic ones. The formation of congeners with a bromine atom in ortho/para- or symmetrical position to the OH group is favored, for the same reasons explained for their chlorinated analogues. Predominance of these congeners was also found in previous studies on thermal degradation of TBBPA containing printed circuit boards (Barontini and Cozzani, 2006; Barontini et al., 2005; Grause et al., 2008).

Fig. 2 shows the congener profiles (relative %) of brominated phenols, where similar formation patterns can be observed for the two samples, so the presence of metals does not seem to have a determining effect on the formation or destruction of these compounds. On the contrary, profiles differ between pyrolysis and combustion experiments. In pyrolysis, 2-BrPh is higher than 3- + 4-BrPh, and 2,6-diBrPh higher than 2,4-diBrPh; this concurs with the formation patterns observed for emissions from the thermal decomposition of tetrabromobisphenol A (Ortuño et al., 2014), which can lead to the formation of these compounds by scission of the molecule. In combustion, however, 3- + 4-BrPh predominates over 2-BrPh, at least at 600 °C that is the

Table 2
Yields of brominated phenols (BrPhs) in pyrolysis and combustion experiments ('P' and 'C' runs) at two different temperatures (600 and 850 °C) for the "WCB" sample (printed circuit board) and the "nmf-WCB" (non-metallic fraction of WCB).

EXPERIMENT	P600		C600		P850		C850	
SAMPLE	WCB	nmf-WCB	WCB	nmf-WCB	WCB	nmf-WCB	WCB	nmf-WCB
COMPOUND	mg compound/kg sample							
2-BrPh	1010	2850	880	2070	3.2	480	–	–
3- + 4-BrPh	37	140	3080	2510	1.5	330	–	–
2,4-diBrPh	16	53	360	260	–	20	–	–
2,3- + 2,5-diBrPh	–	–	–	–	–	–	–	–
2,6-diBrPh	210	770	110	570	–	4.8	–	–
3,5-diBrPh	–	0.21	2.0	5.8	–	–	–	–
3,4-diBrPh	–	–	–	–	–	–	–	–
2,3,5-triBrPh	–	–	0.21	0.62	–	0.06	0.03	–
2,4,6-triBrPh	9.2	25	30	120	–	0.25	0.22	0.25
2,3,4-triBrPh	–	–	0.46	1.33	–	–	–	–
2,4,5-triBrPh	–	–	0.26	0.66	–	–	0.04	–
2,3,6-triBrPh	–	–	0.21	0.82	–	–	0.06	–
3,4,5-triBrPh	–	–	0.11	0.21	–	–	–	–
2,3,5,6-tetraBrPh	–	–	0.14	0.28	–	–	–	–
2,3,4,5- + 2,3,4,6-tetraBrPh	–	–	1.28	1.70	–	–	–	–
pentaBrPh	–	–	0.30	0.29	–	–	–	–
TOTAL	1280	3840	4470	5540	4.7	830	0.35	0.25

(–): not detected or < 0.01 mg/kg sample

temperature where these compounds are observed. With respect to the dibromophenols, the behavior is not clear, as the presence of oxygen and metals could influence different reactions as the TBBPA cracking and the halogenation of phenol. Evans et al. (Evans and Dellinger, 2005) explained the formation of dibromophenols by Br[•] attack at the ortho/para carbon sites of phenoxy or bromophenoxy radicals.

Nevertheless, it is clear that an increase in the temperature promotes the destruction of such pollutants in the presence of oxygen, and the amounts formed are very low, as expected (Conesa et al., 2009).

3.5. PCDD/Fs, dl-PCBs and PBDD/Fs

Due to the toxicity of the compounds presented in this section (see Table 3), all nondetects of dl-PCB and 2,3,7,8-substituted PCDD/Fs and PBDD/Fs were set to their detection limit (LOD), providing for an upper bound of the emission. Reported data for brominated dioxins and furans include the results of the isomer specific analysis and the "Total" values (considering all congeners, not only the toxic ones). Recently, a joint expert panel from the World Health Organization (WHO) and United Nations Environment Programme (UNEP) proposed the use of similar interim Toxic Equivalency Factors (TEF) for chlorinated and brominated dioxins, so WHO₂₀₀₅-TEF values were used to calculate the total toxic equivalency (TEQ) of the samples (van den Berg et al., 2006, 2013).

Respect to the PBDD/Fs emissions, in pyrolysis experiments there are not significant differences between the runs performed at different temperatures, but only total TBDF and TBDD show big differences. In this way, the pyrolysis at 600 °C is producing a lot more of these species than the pyrolysis at 850 °C. This would show the lower thermal stability of the less halogenated species, as has been pointed out in different studies in the case of PCDD/Fs.

Regarding 2,3,7,8-brominated congeners, the amounts obtained in pyrolysis are quite low and very similar at both temperatures. The emissions are 3-fold higher in combustion at 850 °C compared to pyrolysis, while a marked increase is observed in the combustion run at 600 °C. In all cases the most abundant congener is 1,2,3,4,6,7,8-HpBDF among furans and also 1,2,3,4,6,7,8-HpBDD among dioxins. However, 2,3,4,7,8-PeBDF and 1,2,3,4,7,8-HxBDF are the furans that contribute most to the toxicity of the emissions, while 2,3,7,8-TBDD and 1,2,3,7,8-PeBDD are those that enhance toxicity the most. Fig. 3 shows the relative profiles of 2,3,7,8-brominated dioxins and furans from the combustion run at 600 °C, where a similar formation pattern can be observed for both samples.

In pyrolysis at 600 °C, the amounts of total brominated dioxins and total brominated furans are similar, as was found in the decomposition of TBBPA under similar experimental conditions (Ortuño et al., 2014), but for the other runs the furan/dioxin ratio is higher than one, as it has been observed in incineration processes (Ebert and Bahadir, 2003; Lemieux et al., 2002; Söderström and Marklund, 2002). The run with the maximum total emission is also the combustion at 600 °C. For this

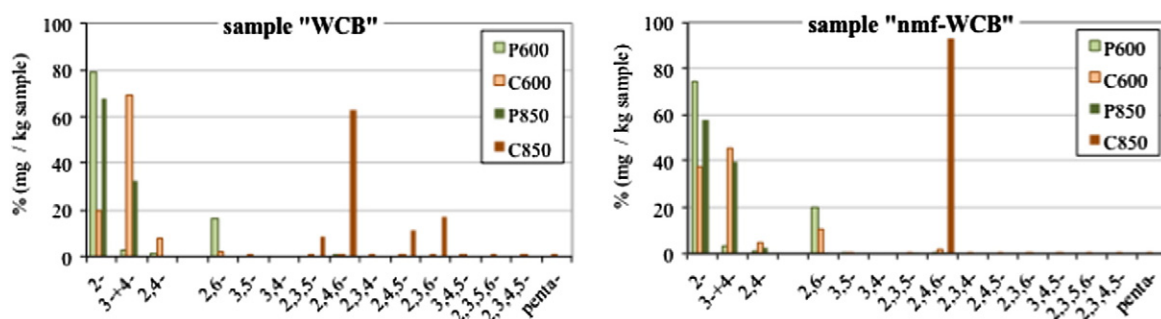


Fig. 2. Congener profiles of brominated phenols during pyrolysis (P) and combustion (C) of printed circuit boards with and without metals ("WCB" and "nmf-WCB" samples) at two different temperatures (600 and 850 °C).

Table 3

PBDD/Fs congeners and summary of 2,3,7,8-PCDD/Fs and dl-PCBs (expressed as ng compound/kg sample, and WHO₂₀₀₅-TEQ values) for the “WCB” and “nmf-WCB” samples in pyrolysis and combustion at 600 and 850 °C.

EXPERIMENT	P600		C600		P850		C850	
SAMPLE	WCB	nmf-WCB	WCB	nmf-WCB	WCB	nmf-WCB	WCB	nmf-WCB
PBDD/Fs								
CONGENERS								
2,3,7,8-TBDF	14	52	6600	4200	28	37	200	340
1,2,3,7,8-PeBDF	66	110	10,800	3000	58	74	220	190
2,3,4,7,8-PeBDF	47	78	3200	1200	42	74	93	150
1,2,3,4,7,8-HxBDF	54	75	16,800	4600	60	96	220	370
1,2,3,4,6,7,8-HpBDF	94	160	19,400	5800	110	180	400	1100
2,3,7,8-TBDD	14	10	1200	1300	14	25	12	25
1,2,3,7,8-PeBDD	40	67	970	410	36	66	53	66
1,2,3,4,7,8 + 1,2,3,6,7,8-HxBDD	27	45	6800	860	30	47	33	47
1,2,3,7,8,9-HxBDD	47	75	4900	670	42	81	34	56
1,2,3,4,6,7,8-HpBDD	60	100	10,700	2000	62	110	66	98
Total 2,3,7,8-PBDFs	280	480	56,800	18,800	300	460	1100	2200
Total 2,3,7,8-PBDDs	190	300	24,600	5200	180	330	200	290
Total 2,3,7,8-PBDD/Fs	470	780	81,400	24,000	480	790	1300	2490
Total WHO ₂₀₀₅ -TEQ PBDD/Fs	85	130	7240	3250	81	140	150	230
HOMOLOGUES								
Total TBDFs	850	2100	53,800	52,400	450	840	1200	1800
Total PeBDFs	110	190	51,500	24,100	100	150	940	2500
Total HxBDFs	54	75	59,600	17,900	60	96	1100	2300
Total HpBDFs	94	160	19,400	5800	110	180	400	1100
Total TBDDs	1200	1900	25,800	23,100	14	25	12	25
Total PeBDDs	40	67	6700	3000	36	66	53	66
Total HxBDDs	73	120	44,500	5300	73	130	67	100
Total HpBDDs	60	100	30,800	11,000	62	110	66	98
Total PBDFs	1100	2500	184,300	100,200	720	1300	3600	7700
Total PBDDs	1400	2200	107,800	42,400	190	330	200	290
Total PBDD/Fs	2500	4700	292,100	142,600	910	1630	3800	7990
PCDD/Fs								
Total 2,3,7,8-PCDFs	170	270	45	130	250	430	160	450
Total 2,3,7,8-PCDDs	190	570	39	110	120	200	140	250
Total 2,3,7,8-PCDD/Fs	360	840	84	240	370	630	300	700
Total WHO ₂₀₀₅ -TEQ PCDD/Fs	18	61	24	47	45	63	31	84
dl-PCBs								
Total PCBs	140	180	240	310	67	350	320	210
Total WHO ₂₀₀₅ -TEQ PCBs	0.92	0.68	2.70	2.50	0.30	0.62	2.10	1.20

run, HxBDFs predominate for the “WCB” sample, with close amounts of TBDFs, PeBDFs and HxBDDs, whereas for the “nmf-WCB” sample, the most abundant homologues are TBDFs. At 850 °C the emission factors are much less than at 600 °C, due to decomposition reactions.

When comparing the emissions from both samples in combustion at 600 °C, the presence of metals in the “WCB” sample significantly promoted PBDD/F formation, as observed by Sakai et al. (Sakai et al., 2001) in a study on combustion of some brominated flame retardants and electronic wastes. Metals catalyze the surface-mediated reaction of precursors (e.g. brominated phenols and other brominated aromatic compounds derived from brominated flame retardants) that lead to the

formation of PBDD/Fs (Duan et al., 2011). However, this effect is not observed for the rest of the runs.

In a previous work (Conesa et al., 2009), a comparison between the emission rates of various pollutants obtained from different wastes was presented, showing that the presence of a small amount of oxygen could promote the formation of different pollutants. Also the formation of PCDD/Fs at intermediate oxygen levels has been found (Conesa et al., 2007). In the present work, the presence of air in substoichiometric condition at low temperature enhances the formation of PBDD/Fs that are easily destroyed at higher temperature in such a way that a lower emission is found at 850 °C.

Some authors have reported the emissions of PBDD/Fs from the thermal treatment of waste printed circuit boards, showing that PBDD/F formation varies widely depending on the tested conditions. Sakai et al. (Sakai et al., 2001) reported emissions of 370 – 14,000 ng/g PBDD/F during incineration of different mixtures of TV casing, PVC and printed circuit boards. Gullett et al. (Gullett et al., 2007) used an open burning test facility in order to simulate rudimentary recycling operations of circuit boards and reported PBDD/F emissions in the mg/kg sample range. Lai et al. (Lai et al., 2007) analyzed the formation of seven 2,3,7,8-brominated congeners in bottom ashes from the pyrolysis of waste WCBs at 850 and 1200 °C and found 1.84 and 0.935 ng/g, respectively. Duan et al. (Duan et al., 2011) analyzed the formation of PBDD/Fs from the incineration of waste printed circuit boards in a low temperature range (250–625 °C) and obtained 160 ng TEQ/kg in the gaseous fraction from the sample heated at 625 °C.

In this study, both for PCDD/Fs and dl-PCBs, the amounts of many of the analyzed congeners were found below or very close to the detection

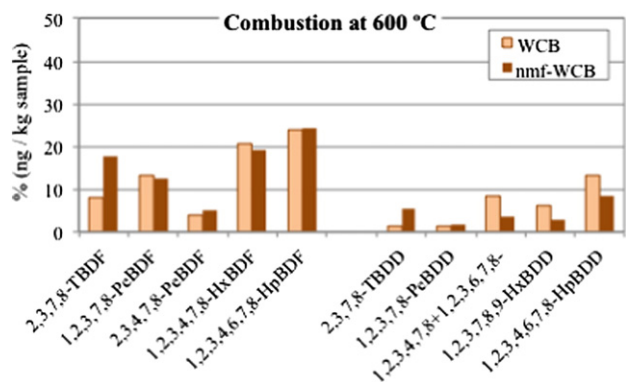


Fig. 3. Congener profile of 2,3,7,8-PBDD/Fs from the combustion at 600 °C of printed circuit boards with and without metals (“WCB” and “nmf-WCB” samples).

limits, probably due to the low sample amounts used in this study and the low chlorine content of the samples. For this reason, it is difficult to deduce any pattern in the formation of these compounds from the present results.

From the results obtained for both samples under the same experimental conditions, it can be concluded that, in general, the emission trends of the compounds evolved depended mainly on operating conditions (temperature and oxygen ratio), but also on the presence of metals in the material.

In previous studies (Moltó et al., 2011, 2009), relatively low emission factors of PCDD/Fs were obtained in the thermal treatment of electronic wastes, and the results observed in this study confirmed this fact. In any case, PBDD/F emissions are significantly higher than those of PCDD/Fs.

4. Conclusions

The emissions generated during the decomposition of printed circuit boards (with and without metals) at two temperatures (600 and 850 °C) and two different atmospheres (nitrogen and sub-stoichiometric air) have been studied.

Besides CO and CO₂, hydrogen bromide is the main gaseous product emitted during the decomposition of the printed circuit boards, increasing its formation with increasing temperature.

For both samples, the most abundant light hydrocarbons are methane, ethylene, benzene and toluene, with higher yields in pyrolytic conditions at 850 °C.

Within the semivolatile compounds, the most abundant are phenol, benzofuran and styrene, detected in all runs, but in the presence of oxygen at 850 °C, when these compounds are oxidized.

Bromophenol emissions are much higher than that of chlorophenols and chlorobenzenes, with the highest yields during combustion at 600 °C. PBDD/F emissions are significantly higher than that of PCDD/Fs and dl-PCBs.

From the results obtained for both samples under the same experimental conditions, it can be concluded that, in general terms, the emission trends of the compounds evolved depended mainly on operating conditions (temperature and oxygen ratio), but also on the presence of metals in the material.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.08.039>.

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